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Manufacture of Water-borne Biopolyurethane Film Based on Caster Oil and Tri Methylol Propane for Leather Coationg

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Abstract : Undenatured castor oil and trimethylolpropane (TMP) were used to obtain bio-based water-based polyurethane. Isophorone diisocyanate (IPDI) was incorporated into the formulation to obtain a transparent film, and ethylenediamine (EDA) was used for chain extension. In order to measure the change in physical properties according to the contents of castor oil and TMP, each tensile strength, elongation, and abrasion resistance test was conducted. As the contents of castor oil and TMP increased, the tensile strength increased, the elongation decreased, and the surface hardened strongly as the respective contents increased.

Keywords: water dispersion, polyurethane, castor oil, trimethylolpropane, leather coating

1. Introduction

Water-based polyurethane (WBPU) has been developed as an alternative to standard polyurethane dissolved in organic solvents to reduce the release of organic volatile components in the application stage for obtaining coatings, paints, or films. The growing public's interest in reducing the harmful effects on the environment is contributing to this development[1]. Most commercially available polyurethane (PU) has still been synthesized from petroleum-based raw materials and over the past few decades, synthesis has been studied using bio-based raw materials to replace petroleum-based raw materials. Biopolyol has been studied in the direction of synthesizing bio-derived chemicals because it is relatively easy to manufacture, and in fact, many diol and polyol based on biomass are currently supplied by several companies[2-4]. Most of these biopolyols are vegetable oils obtained from various plants and undergo chemical transformation, with different structural polyols giving different final properties to different structural derivatives (PUs)[5-8]. Among vegetable oils, castor oil naturally has an OH group in its molecular structure, which is advantageous to choose as a bio-based raw material (no pretreatment required) for use in polyurethane production.

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Castor oil-based water-dispersible polyurethane (CPUD) is prepared by reaction of diol or polyol with aliphatic isocyanate, which is less reactive with water than aromatic isocyanate, and in certain cases isophoron diisocyanate (IPDI) gives transparency to the prepared film[9,10]. The CPUD must essentially be formed into a stable suspension in an aqueous medium, which serves as the reason why the formulation must include an emulsifier. Internal emulsifiers, chemically bonded to form part of the PU structure, are preferred because they make more stable suspensions compared to PUs obtained with external emulsifiers. Since external emulsifiers generally require the use of strong shear forces for mixing, dispersed colloidal particles are unstable, resulting in low storage stability [11-13]. The internal emulsifier, on the other hand, consists of diol introducing ionic groups (anionic or cationic) into the chemical structure of polyurethane. Diol reacts with isocyanate and further addition of opposite ions may form a salt allowing stabilization of the polyurethane water suspension. The emulsifier applied to acidic diol is a petroleum-based reactant, DMPA (dimethylol propionate), which is neutralized by the addition of a base such as triethylamine (TEA) to impart anion[14-15]. The water- dispersed form of the anionic prepolymer produced at this time is stable at room temperature (20-30℃), and the IPDI used in urethane synthesis has slow synthesis with OH at room temperature, making it easy to adjust the water-dispersed polyurethane resin in this study.

The cohesiveness of urethane to improve the mechanical properties of resin film was improved to apply a water-dispersible polyurethane coating agent to the surface of Lamleather, and to this end, the four-day extension reaction was applied. Ethylene diamine (EDA) was applied as the chain extender used.

This study analyzed the properties of water-dispersed polyurethane coating agents in two types, first, the changes in water-dispersed polyurethane properties according to the content of castor oil, and second, the properties of coating agents according to the content of TMP.

2. Experiment

2.1. Material

First, the reagents used for the synthesis of water-dispersed polyurethane are castor oil, polypropylene glycol (PPG, molecular weight 1000, BASF), isophororne diisocyanate (IPDI, Bayer), dimethylolpropionic acid (DMPA, GEO), aceton (Aldrich) , dibutyltin dilaurate (DBTDL, Aldrich), trimethylolpropane (TMP, Aldrech), triethylamine (TEA, Fluka), and ethylene diamine (EDA, Fluka) were used.

2.2. Instrument

Simultaneous DSC-TGA(SDT Q50, TA Instr., U.S.A), UTM(Universal testing machine, Instron Co., U.S.A.), electron microscope (TW-ST-XZM-2, Chung Buk TEC), Taber abrasion tester(TO 880T, Test One)

2.3.1. Synthesis of water-dispersed polyurethane resin containing castor oil and TMP

First, for the synthesis of a sample (water-dispersed polyurethane) for the analysis of water-dispersed polyurethane resin (CPUD) according to castor oil, nitrogen is substituted at 60℃ to remove moisture in a 4-hole flask and heated for 30 minutes. Thereafter, castor oil(1wt%, 3wt%, 5wt%, 7wt%), PPG, aceton, and DMPA are added and stirred at 60℃ for 1 hour under a nitrogen atmosphere. In the next step, IPDI and DBTDL were slowly added to the flask, and then reacted at 90℃ to 95℃ for 3 hours. Thereafter, the reaction tank was cooled to 35℃ to 40℃, and then TEA was added to complete neutralization. After the neutralized resin was slowly added with distilled water in a high-speed stirring state to disperse water, EDA was slowly dripped with distilled water for chain extension, and the chain extension reaction was stably performed. Thereafter, the synthesis was completed by stirring for 1 hour while maintaining the temperature (Table 1). The second sample, CPUD-tmp, was synthesized by correcting the wt% of the sample (CPUDC) used in the prepolymer in the first sample and applying the content of TMP to increase the crosslinking density at 1 wt%, 2 wt%, 3 wt%, and 4 wt%.

3. Results and considerations

3.1. Physical Properties Measurement Analysis

In order to measure the tensile strength, elongation, and wear resistance of the prepared sample (film), 20g was measured on a chare, dried naturally for 12 hours, and then heat-dried at 120℃ for 1hr to form a 50mm wide, 100mm long, and 0.3mm thick film. In the sample for measuring the wear resistance mechanical properties, the resin synthesized on the leather surface was roll-coated to a thickness of 0.1 mm, dried at room temperature for 12 hours, and dried at 80℃ for 5 hours. The weight of the specimen was measured according to the ASTM 1175 test method, and the reduced weight was measured after 2,000 cycles were rotated with Wheel number CS-10 by abrasion resistance measuring equipment. Samples for analysis of tensile strength and physical properties of elongation were prepared with a thickness of 012 mm and a width of 150 mm, and then stretched at a tensile speed of 100 ± 20 mm/min by a tensile tester.

Figure 1 shows the results of measuring the tensile strength of samples with different synthesis ratios of castor oil. According to the presented measurement results, the tensile strength of the sample CPUD-1 prepared with 1g of castor oil was 0.98 kgf/㎟, and the tensile strength of the sample CPUD-4 prepared with 7g of synthesis was 1.51 kgf/㎟. As such, it was confirmed that the tensile strength increased as the synthesis ratio of castor oil increased. It is believed that as the

Table 1. The compounds used in Castor oil-based water-dispersible polyurethane(CPUD)

Sample	PPG(g)	CASER OIL(g)	IPDI(g)	EDA(g)
CPUD-1	39	1	40	1
CPUD-2	37	3	40	1
CPUD-3	35	5	40	1
CPUD-4	33	7	40	1

Table 2. The compounds used in Castor oil-based water-dispersion polyurethane with different TMP content(CPUD-tmp)

Sample	PPG(g)	CASER OIL(g)	IPDI(g)	TMP	EDA(g)
CPUD-tmp1	30	10	40	1	1
CPUD-tmp2	30	10	40	2	1
CPUD-tmp3	30	10	40	3	1
CPUD-tmp4	30	10	40	4	1

content of castor oil relative to PPG increased, the molecular weight decreased, the particle size between the average particles decreased, and the crosslinking reaction of the chain was affected by castor oil with three reactors.

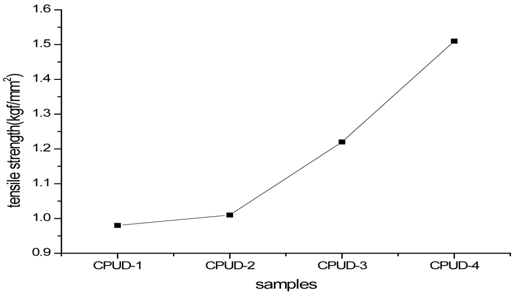


Fig. 1. Tensile strength measurement result of polyurethane resin with different Castor oil composition ratio.

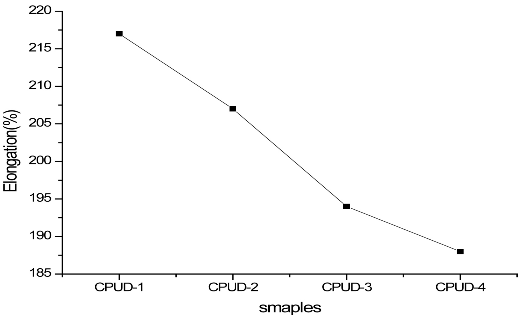


Fig. 2. Elongation measurement result of polyurethane resin with different Castor oil composition ratio.

Fig. 2 shows the results of measuring the elongation of samples with different synthesis ratios of castor oil. According to the presented measurement results, the elongation was measured at 217% in the case of the sample CPUD-1 prepared with 1g of castor oil, and the elongation was measured at 188% in the case of the sample CPUD-4 prepared with 7g of synthesis. As such, it was confirmed that the elongation rate decreased as the synthesis ratio of castor oil increased. As the content of castor oil relative to PPG increases, the molecular weight decreases, the particle size of the average particle decreases, and the crosslinking reaction of the chain is strong due to the influence of castor oil with three reactors, elongation performance was decreased.

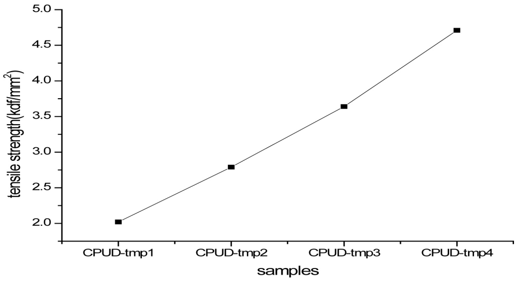


Fig. 3. Tensile strength measurement result of polyurethane resin with different TMP composition ratio.

Figure 3 shows the results of measuring the tensile strength of samples with different synthesis ratios of TMP. According to the presented measurement results, the tensile strength of the sample CPUD-tmp1 prepared with a synthesis ratio of TMP of 1g was 2.02 kgf/㎟, and the tensile strength of the sample CPUD-tmp4 prepared with a synthesis ratio of 4g was 4.71 kgf/㎟. As such, as the synthesis ratio of TMP increases, the tensile strength increases. It can be inferred that as the content of TMP increases, the physical tensile strength was increased as the density of the crosslinking reaction increases.

Figure 4 shows the measurement results of the elongation of the water-dispersed polyurethane sample with different synthesis ratios of TMP. According to the presented measurement results, the elongation was measured to be 174% in the case of sample CPUD-tmp1 prepared with a synthesis ratio of TMP of 1g, and the elongation was measured to be 144% in the case of sample CPUD-tmp4 prepared with a synthesis ratio of 4g. As the synthesis ratio of TMP increases, the elongation decreases, which is believed to be due to the crosslinking reaction of TMP with three reactors in soft segment cohesion in chain extension, which is the final stage of water-dispersible polyurethane synthesis.

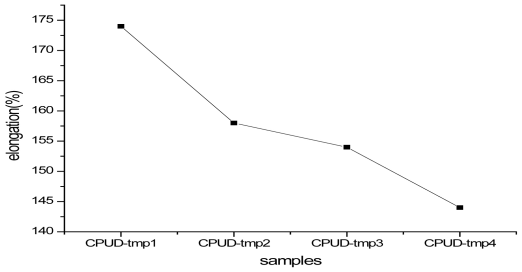
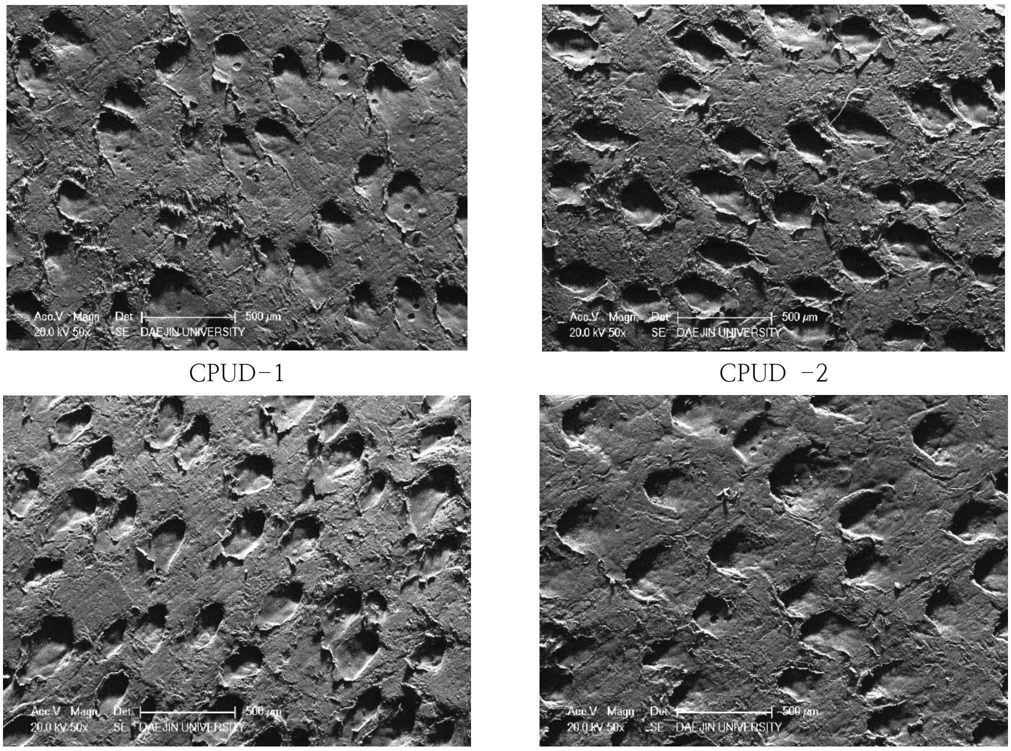


Fig. 4. Elongation measurement result of polyurethane resin with different TMP composition ratio.

Figure 5 presents the results of measuring wear resistance to measure the surface strength of water-dispersed polyurethane samples with different synthetic ratios of castor oil.

For the measurement of abrasion resistance, the weight of the test specimen was measured according to the ASTM 1175 test method using a Taber abrasion tester (TO 880T, Test Center), by 1,000 cycles with Wheel number CS-10, and then scanning electron microscope (SEM) was used to visually check the destruction of the worn surface. As can be seen with the naked eye, it was confirmed that the CPUD-4 sample with a high synthesis ratio of castor oil had the lowest degree of surface destruction. Similar to the tensile strength, the more OH groups of castor oil involved in the synthesis of the prepolymer, the more reactive groups that act on the bond with amine for chain extension are distributed, which is interpreted as the result of the higher



CPUD-1 CPUD -2

CPUD -3 CPUD -4

Fig. 5. Abration resistance measurement result of polyurethane resin with different Castor oil composition ratio by SEM.

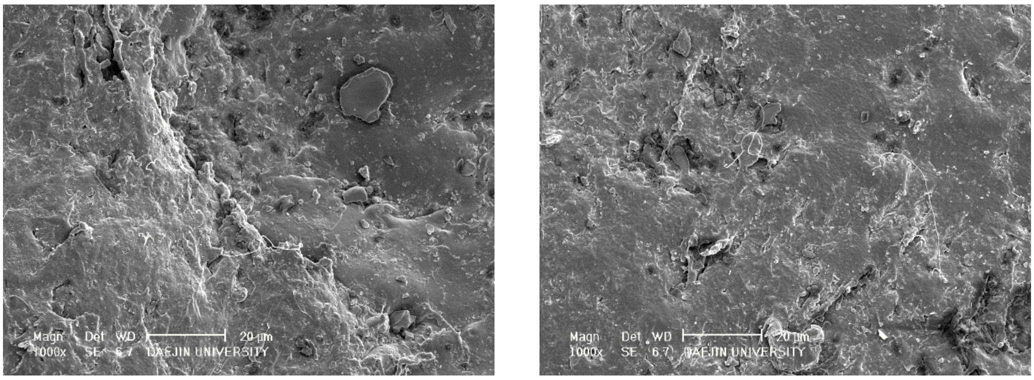
cohesiveness of the chain.

In Fig. 6, wear resistance of water-dispersed polyurethane in accordance with the TMP synthesis ratio was measured in the same manner as in Fig. 5, and the results were confirmed using SEM. According to the photographed surface, the higher the ratio of OH groups of TMP involved in synthesis, the more reactors to act on binding with amine for chain extension are distributed, and thus, CPUD-tmp4 has the lowest surface change.

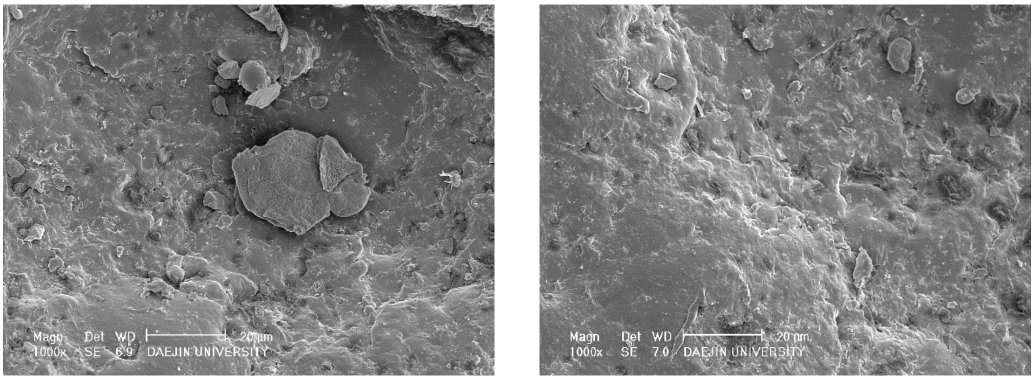
4. Conclusion

For this studyBasically, polypropylene glycol (PPG), trimethylolpropane (TMP), castor oil, isoprone diisocynate (IPDI), and dimethylolpropionic acid (DMPA) were reacted as starting materials, neutralized with TEA, and dispersed in water, and then the moist polyurethane resin was synthesized through a chain extension reaction.

As a result of the tensile strength test, the polyurethane film containing a lot of castor oil showed high tensile strength. This is because the higher the ratio of the NCO group of isocyanate reacting to the OH group of the polyol, the more the number of reactive groups involved in chain extension increases and the degree of cohesion increases It was inferred that the tensile strength increased as a result. Conversely, as a result of measuring the elongation rate, the higher the castor oil



CPUD-tmp 1 CPUD-tmp 2



CPUD-tmp 3 CPUD-tmp 4

Fig. 6. Abration resistance measurement result of polyurethane resin with different TMP composition ratio by SEM.

content, the lower the elongation rate, and the result contradicting the tensile strength.

Next, it was found that the tensile strength also increased as the content ratio of TMP increased. Conversely, in the case of the elongation, a decrease in the elongation rate was confirmed as the density of the chain increased.

The surface strength of the resin according to the content ratio of castor oil and TMP is as follows. The surface strength increased as the degree of agglomeration due to chain extension increased as the cast oil increased. In addition, it was confirmed that the surface strength also increased as the content ratio of TMP increased.

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